



# The effect of quaternary ammonium on discharge characteristic of a non-aqueous electrolyte Li/O<sub>2</sub> battery

Sheng S. Zhang\*, Donald Foster, Jeffrey Read

U.S. Army Research Laboratory, RDRL-SED-C, 2800 Powder Mill Road, Adelphi, MD 20783-1197, USA

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## ABSTRACT

The effect of quaternary ammonium on discharge characteristic of Li/O<sub>2</sub> cells was studied by using Super-P carbon as air cathode, a 0.2 mol kg<sup>-1</sup> LiSO<sub>3</sub>CF<sub>3</sub> 1:3 (wt.) PC/DME solution as baseline electrolyte, and tetrabutylammonium triflate (NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub>) as an electrolyte additive or a co-salt. Results show that Li/O<sub>2</sub> cells can run normally in an electrolyte with NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> as the sole conductive salt. However, such cells suffer lower voltage and capacity as compared with those using the lithium ionic baseline electrolyte. This is due to the larger molar volume of quaternary ammonium cation, which results in less deposition of oxygen reduction products on the surface of carbon. When used as an electrolyte additive or a co-salt, the ammonium is shown to increase capacity of Li/O<sub>2</sub> cells. The plot of differential capacity versus cell voltage shows that the Li/O<sub>2</sub> cell with ammonium added has broad and scattered differential capacity peaks between the voltages of two reactions of “2Li + O<sub>2</sub> → Li<sub>2</sub>O<sub>2</sub>” and “2Li + Li<sub>2</sub>O<sub>2</sub> → 2Li<sub>2</sub>O”. This phenomenon can be attributed to the phase transfer catalysis (PTC) property of quaternary ammonium on the second reaction. Due to inverse effects of the cation geometric volume and the PTC property of ammonium ions on the discharge capacity, there is an optimum range for the concentration of ammonium. It is shown that the addition of NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> increases discharge capacity of Li/O<sub>2</sub> cell only when its concentration is in a range from 5 mol% to 50 mol% vs. the total of Li/ammonium mixed salt, and that the optimum concentration is about 5 mol%. In this work we show that the addition of 5 mol% NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> into the baseline electrolyte can increase discharge capacity of a Li/O<sub>2</sub> cell from 732 mAh g<sup>-1</sup> to 1068 mAh g<sup>-1</sup> (in reference to the weight of Super-P carbon) when the cell is discharged at 0.2 mA cm<sup>-2</sup>.

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## 1. Introduction

Non-aqueous electrolyte Li/air batteries are unique in that their discharge products are insoluble in the electrolyte [1–16]. In discharge, oxygen dissolved in liquid electrolyte is catalytically reduced on the surface of carbon air cathode into peroxide or oxide anions that instantly combine with Li<sup>+</sup> ions in the liquid electrolyte to form insoluble lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) and lithium oxide (Li<sub>2</sub>O). In such cells, the oxygen reduction is a typical liquid–solid heterogeneous reaction. Due to the insolubility of Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>O, these oxygen reduction products are directly deposited on the surface of carbon, and clog the access of oxygen to the reaction sites. Therefore, the amount that the oxygen reduction products can be deposited on the surface of carbon becomes the main factor to determine the discharge capacity of a Li/air cell, and the specific capacity of a Li/air cell is often referred to the weight of carbon [1,2]. In previous work [15], we have shown that a liquid–solid (i.e., electrolyte–carbon) “two-phase reaction zone” is needed for

maximizing the specific capacity of carbon. To meet high power capability, meanwhile, the thickness of liquid electrolyte film on the surface of carbon should remain as thin as possible so that the diffusion distance of the dissolved oxygen can be minimized. An ideal status of the liquid electrolyte in Li/air cells is that the electrolyte is able to wet the surface of carbon completely while with the minimized amount of liquid electrolyte. Most of previous efforts on these batteries were focused on optimizing electrolyte formulation [2,3,5,10,11,12], increasing carbon porosity [13,14], and improving the design of air electrode [2,6,8,9] so that the maximized amount of oxygen reduction products can be deposited on the surface of carbon.

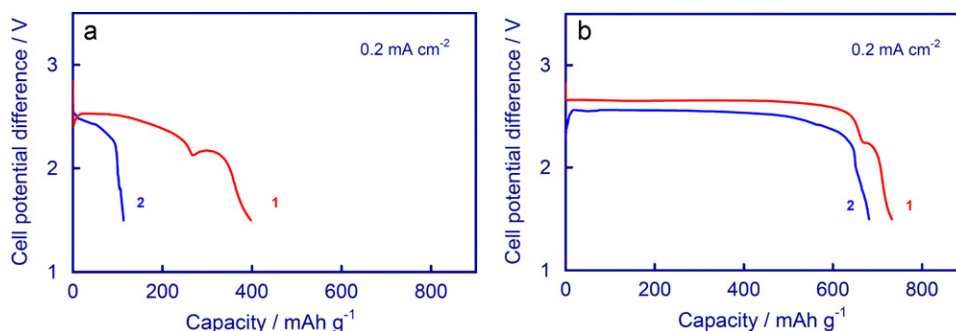
In organic synthesis, quaternary ammonium salts are often used as the phase transfer catalyst (PTC) to promote heterogeneous reactions [17]. In reaction, ammonium cations facilitate the movement of poorly soluble reactants from solid phase into solution phase where the reaction occurs. Based on a similar principle, in this work we propose tetrabutylammonium triflate (NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub>) as an additive or a co-salt of the non-aqueous electrolyte to improve the discharge characteristic of Li/O<sub>2</sub> cells. It is assumed that in oxygen reduction, the ammonium cations can combine peroxide anions to form slightly soluble tetrabutylammonium per-

\* Corresponding author. Tel.: +1 301 394 0981; fax: +1 301 394 0273.

E-mail address: [szhang@arl.army.mil](mailto:szhang@arl.army.mil) (S.S. Zhang).

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14. ABSTRACT <b>The effect of quaternary ammonium on discharge characteristic of Li/O2 cells was studied by using Super-P carbon as air cathode, a 0.2 mol kg<sup>-1</sup> LiSO3CF3 1:3 (wt.) PC/DME solution as baseline electrolyte, and tetrabutylammonium triflate (NBu4SO3CF3) as an electrolyte additive or a co-salt. Results show that Li/O2 cells can run normally in an electrolyte with NBu4SO3CF3 as the sole conductive salt. However, such cells suffer lower voltage and capacity as compared with those using the lithium ionic baseline electrolyte. This is due to the larger molar volume of quaternary ammonium cation, which results in less deposition of oxygen reduction products on the surface of carbon. When used as an electrolyte additive or a co-salt, the ammonium is shown to increase capacity of Li/O2 cells. The plot of differential capacity versus cell voltage shows that the Li/O2 cell with ammonium added has broad and scatted differential capacity peaks between the voltages of two reactions of 2Li + O2 → Li2O2 and 2Li + Li2O2 → 2Li2O. This phenomenon can be attributed to the phase transfer catalysis (PTC) property of quaternary ammonium on the second reaction. Due to inverse effects of the cation geometric volume and the PTC property of ammonium ions on the discharge capacity, there is an optimum range for the concentration of ammonium. It is shown that the addition of NBu4SO3CF3 increases discharge capacity of Li/O2 cell only when its concentration is in a range from 5 mol% to 50 mol% vs. the total of Li/ammonium mixed salt, and that the optimum concentration is about 5 mol%. In this work we show that the addition of 5 mol% NBu4SO3CF3 into the baseline electrolyte can increase discharge capacity of a Li/O2 cell from 732mAhg<sup>-1</sup> to 1068mAhg<sup>-1</sup> (in reference to the weight of Super-P carbon) when the cell is discharged at 0.2mAcm<sup>-2</sup>.</b>		
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**Fig. 1.** Discharge curves of Li/O<sub>2</sub> cells with an electrolyte having (1) a LiSO<sub>3</sub>CF<sub>3</sub> lithium salt and (2) an NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> quaternary ammonium, respectively, as the conductive salt. (a) 0.2 mol kg<sup>−1</sup> salt in PC and (b) 0.2 mol kg<sup>−1</sup> salt in a 1:3 PC/DME mixed solvent.

oxide, (NBu<sub>4</sub>)<sub>2</sub>O<sub>2</sub>, which is believed to change the morphology of Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>O precipitates on the surface of carbon and promote the reaction of “2Li + Li<sub>2</sub>O<sub>2</sub> → 2Li<sub>2</sub>O”. We here evaluate and discuss the effect of NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> on the discharge behavior of Li/O<sub>2</sub> cells.

## 2. Experimental

Lithium triflate (LiSO<sub>3</sub>CF<sub>3</sub>, 96%) and tetrabutylammonium triflate (NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub>, >99.0%) were purchased from Aldrich and dried at 100 °C under vacuum for 8 h prior to use. N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR<sub>14</sub>TFSI, a room temperature ionic liquid) was kindly provided by Prof. W.A. Henderson of the U.S. Naval Academy. A carbon air cathode with a composition of 90% Super-P carbon and 10% polytetrafluoroethylene (PTFE) was prepared by mixing calculated amounts of Super P and PTFE emulsion (Teflon®, solid content = 61.5%, DuPont Co.) and rolling the mixed paste into a free-standing cathode sheet. Typically, the air cathode has a thickness of 0.5–0.6 mm and a porosity of 2.9–3.2 cm<sup>3</sup> g<sup>−1</sup> (vs. Super P). Detailed descriptions on the preparation of air cathode can be referred to our previous papers [2,3,5]. The air cathode sheet was punched into small disks with an area of 0.97 cm<sup>2</sup>, followed by drying at 100 °C under vacuum for at least 8 h. Using a 1:3 (wt.) blend of propylene carbonate (PC, electrolyte grade, Ferro) and 1,2-dimethoxyethane (DME, electrolyte grade, Ferro) as the solvent, a 0.2 mol kg<sup>−1</sup> LiSO<sub>3</sub>CF<sub>3</sub> 1:3 PC/DME solution was prepared as the baseline electrolyte in a glove-box. Under the same condition, other electrolytes with NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> or PYR<sub>14</sub>TFSI as the additive/co-salt were prepared by mixing calculated amounts of salts and solvent blend.

In a dry-room having a dew point of below −90 °C, Li/air cells with an air window of 0.97 cm<sup>2</sup> were assembled by stacking a Li foil, a Celgard® 3500 membrane, a carbon air cathode, a Ni mesh as the current collector, and an air window in sequence into a coin cell cap. To activate the cell, 200 μL of liquid electrolyte was added through the air-window, followed by applying a vacuum for 20 s to ensure complete wetting. Extra liquid electrolyte was removed by lightly swiping a filter paper on the top of Ni mesh. The electrolyte-activated cell was clamped on a cell holder and sealed in an O<sub>2</sub>-filled plastic bag. Detailed procedures for the assembly of Li/O<sub>2</sub> cells were described in our previous papers [15,16]. After assembly, the Li/O<sub>2</sub> cells were rested for 2 h to reach the equilibrium of oxygen concentration between the air cathode and O<sub>2</sub> in the bag, followed by discharging on a Maccor Series 4000 cycler with a 1.5 V cutoff voltage. Unless otherwise stated, the discharge was performed at room temperature (~22 °C) with a fixed current rate of 0.2 mA cm<sup>−2</sup>.

## 3. Results and discussion

### 3.1. Li/O<sub>2</sub> cell with ammonium as sole conductive salt

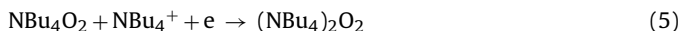
In non-aqueous electrolytes, catalytic reduction of oxygen on the surface of carbon is generally processed through a two-electron process. That is, oxygen dissolved in the electrolyte is reduced to form peroxide anion (O<sub>2</sub><sup>2−</sup>) that instantly combines with cations (M<sup>+</sup>) in the liquid electrolyte to form peroxide (M<sub>2</sub>O<sub>2</sub>), which can be written as Eqs. (1) and (2), respectively:



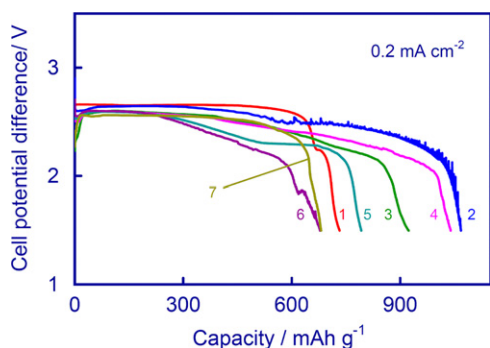
Depending on discharge current rate and electrolyte formulation, the resulting M<sub>2</sub>O<sub>2</sub> can be further reduced into oxide (M<sub>2</sub>O) at lower potentials as described by Eq. (3) [15]:



As shown in Eqs. (1)–(3), these reactions do not have to be supported by a Li<sup>+</sup> ionic electrolyte. Laoire et al. [18,19] recently reported that a stable tetrabutylammonium peroxide, (NBu<sub>4</sub>)<sub>2</sub>O<sub>2</sub>, can be formed irreversibly by oxygen reduction in a tetrabutylammonium organic solution through two steps:



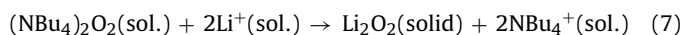
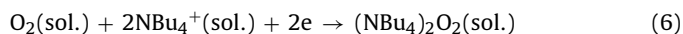
where Eq. (4) is highly reversible while Eq. (5) is irreversible. In this work we attempt to use NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> as a sole salt for the electrolyte of Li/O<sub>2</sub> cells and evaluate the discharge characteristic of such cells. Fig. 1 compares discharge curves of Li/O<sub>2</sub> cells with a LiSO<sub>3</sub>CF<sub>3</sub> and a NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> electrolyte, respectively. It is shown that the Li/O<sub>2</sub> cells can run normally in a NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> electrolyte. However, the cells with NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> electrolyte suffer lower discharge voltage and less capacity. The former is due to a better merge of the voltages of two discharge stages corresponding to Reaction-1 and Reaction-3 in the NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> electrolyte, which results in a lower averaged voltage. However, the discharge voltages of Reaction-1 and Reaction-3 are well separated in the LiSO<sub>3</sub>CF<sub>3</sub> electrolyte, resulting in two voltage plateaus as indicated by Curve-1 in Fig. 1a and b. On the other hand, the lower capacity of Li/O<sub>2</sub> cells in NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> electrolyte than in LiSO<sub>3</sub>CF<sub>3</sub> electrolyte is due to the large molar volume of ammonium cation, which results in less deposition of the oxygen reduction products (M<sub>2</sub>O<sub>2</sub> and M<sub>2</sub>O, where M represents ammonium cation) on the surface of carbon. By comparing Fig. 1a and b, we see that the effect of NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> ammonium on the discharge behavior of Li/O<sub>2</sub> cells is more negative in the highly viscous PC solution.



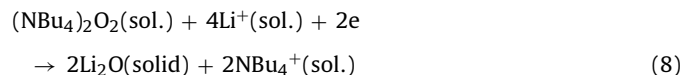
**Fig. 2.** Effect of  $\text{NBu}_4\text{SO}_3\text{CF}_3$  on the discharge capacity of  $\text{Li}/\text{O}_2$  cells with a  $0.2 \text{ mol kg}^{-1}$   $[(1-x)\text{LiSO}_3\text{CF}_3 - x\text{NBu}_4\text{SO}_3\text{CF}_3]$  1:3 PC/DME electrolyte. (1)  $x=0$ , (2)  $x=0.05$ , (3)  $x=0.20$ , (4)  $x=0.50$ , (5)  $x=0.60$ , (6)  $x=0.80$ , and (7)  $x=1.0$ .

### 3.2. $\text{Li}/\text{O}_2$ cell with ammonium as electrolyte additive or co-salt

Fig. 2 shows the effect of  $\text{NBu}_4\text{SO}_3\text{CF}_3$  concentration on the discharge characteristic of  $\text{Li}/\text{O}_2$  cells in an electrolyte consisting of a  $0.2 \text{ mol kg}^{-1}$   $\text{LiSO}_3\text{CF}_3$ – $\text{NBu}_4\text{SO}_3\text{CF}_3$  mixed salt dissolved in a 1:3 (wt.) PC/DME blend. Generally, the lower voltage plateau reflecting Eq. (3) cannot be well defined in the cells with ammonium as the additive or co-salt. This could be associated with the slight solubility of ammonium peroxide,  $(\text{NBu}_4)_2\text{O}_2$ , in organic electrolyte. In the presence of low concentration of  $\text{NBu}_4\text{SO}_3\text{CF}_3$  ammonium, the oxygen reduction can take place as follows:

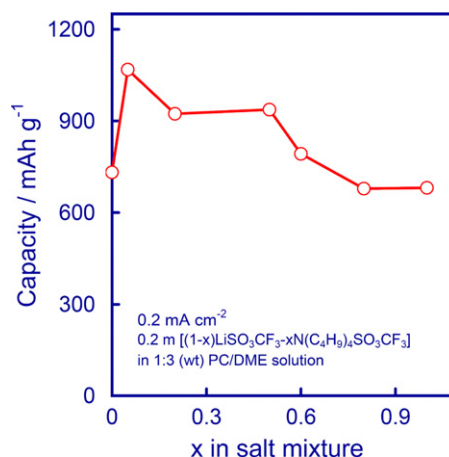


or



where Eqs. (7) and (8) involve a cation exchange reaction between  $\text{NBu}_4^+$  cation and  $\text{Li}^+$  ion. Due to significantly lower solubility of  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$  than  $(\text{NBu}_4)_2\text{O}_2$ , reactions (7) and (8) are expected to occur instantly. Even in the presence of small amount of  $\text{Li}^+$  ions,  $(\text{NBu}_4)_2\text{O}_2$  can be readily transferred into  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$  [18,19]. Therefore, the ammonium cation not only facilitates Eq. (3) to reduce discharge polarization, but also favors the growth of final discharge products in particle size and gravity density. The reduction in discharge polarization results in a good merge of two discharge voltage plateaus reflecting Eqs. (1) and (3), respectively.

Fig. 3 exhibits a relationship of the discharge capacity of  $\text{Li}/\text{O}_2$  cells with the concentration of  $\text{NBu}_4\text{SO}_3\text{CF}_3$  ammonium in mixed salts. It is shown that a small addition (5 mol%) of  $\text{NBu}_4\text{SO}_3\text{CF}_3$  can significantly increase the capacity of  $\text{Li}/\text{O}_2$  cell. Further increase in

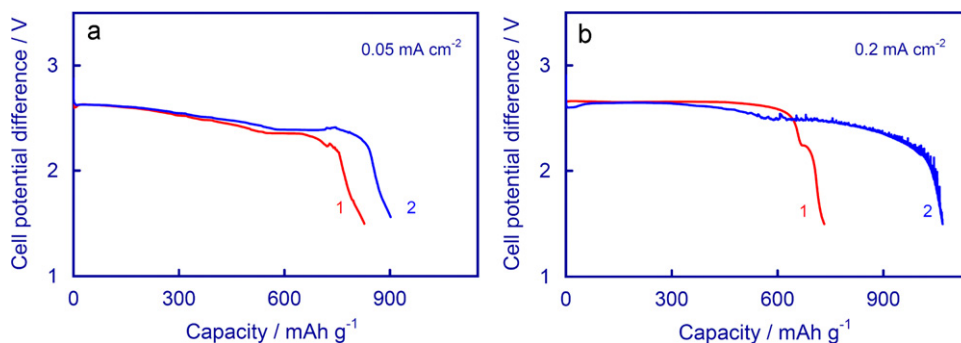


**Fig. 3.** Discharge capacity of  $\text{Li}/\text{O}_2$  cells as a function of the concentration of  $\text{NBu}_4\text{SO}_3\text{CF}_3$  in an electrolyte consisting of  $0.2 \text{ mol kg}^{-1}$   $[(1-x)\text{LiSO}_3\text{CF}_3 - x\text{NBu}_4\text{SO}_3\text{CF}_3]$  1:3 PC/DME.

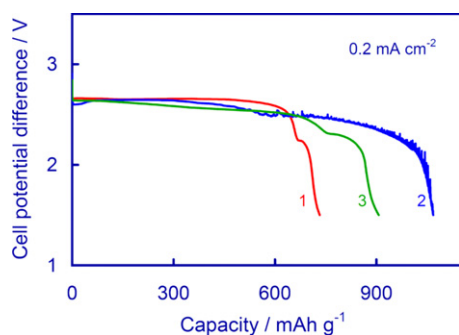
the concentration reduces the improvement efficiency of ammonium on the discharge capacity. When the concentration exceeds 60 mol%, the effect of ammonium on the capacity of  $\text{Li}/\text{O}_2$  cells becomes negative. These phenomena can be attributed to the other effect of ammonium. That is, Reactions (6)–(8) improve the morphology of the oxygen reduction products ( $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$ ), resulting in more dense deposition. When the ammonium becomes a major salt in the electrolyte, part of the oxygen reduction products may be deposited in the form of  $(\text{NBu}_4)_2\text{O}_2$ . Due to significantly larger volume of  $\text{NBu}_4^+$  cation than  $\text{Li}^+$  ion, the total amounts that  $(\text{NBu}_4)_2\text{O}_2$  and  $\text{Li}_2\text{O}_2$  can deposit on the surface of carbon are reduced, resulting in lower capacity.

Fig. 4 compares discharge curves of the  $\text{Li}/\text{O}_2$  cells without and with the addition of 5 mol%  $\text{NBu}_4\text{SO}_3\text{CF}_3$  in a PC and a 1:3 PC/DME based electrolyte, respectively. The improvement in discharge capacity can be observed from both cases. In particular, Fig. 4b shows that the capacity of  $\text{Li}/\text{O}_2$  cell in a 1:3 PC/DME electrolyte is increased to  $1068 \text{ mAh g}^{-1}$  from  $732 \text{ mAh g}^{-1}$  of the baseline electrolyte (both were at  $0.2 \text{ mA cm}^{-2}$  and referred to the weight of Super-P) as a result of the addition of 5 mol%  $\text{NBu}_4\text{SO}_3\text{CF}_3$ . It seems that the major difference in the discharge characteristic between electrolytes without and with  $\text{NBu}_4\text{SO}_3\text{CF}_3$  ammonium occurs in the lower voltage plateau corresponding to Eq. (3). As shown in Fig. 4b, the lower voltage plateau of Cell-2 with 5 mol%  $\text{NBu}_4\text{SO}_3\text{CF}_3$  not only is longer but also has higher voltages, as compared with that of Cell-1.

Eqs. (2) and (3) do not suggest a specific structure for the ammonium cation. Theoretically, all quaternary ammoniums have similar functions. To confirm this, we examine N-



**Fig. 4.** The effect of quaternary ammonium on the discharge capacity of  $\text{Li}/\text{O}_2$  cells in different electrolytes, where (1) baseline and (2) baseline + 5 mol%  $\text{NBu}_4\text{SO}_3\text{CF}_3$ . (a)  $0.2 \text{ mol kg}^{-1}$   $\text{LiSO}_3\text{CF}_3$  PC as baseline at  $0.05 \text{ mA cm}^{-2}$  and (b)  $0.2 \text{ mol kg}^{-1}$   $\text{LiSO}_3\text{CF}_3$  1:3 PC/DME as baseline at  $0.2 \text{ mA cm}^{-2}$ .

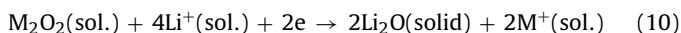
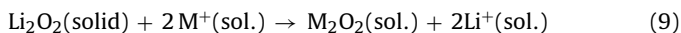


**Fig. 5.** Comparison of the effect of organic ammoniums on the discharge capacity of Li/O<sub>2</sub> cells. (1) Baseline electrolyte consisting of a 0.2 mol kg<sup>-1</sup> LiSO<sub>3</sub>CF<sub>3</sub> 1:3 PC/DME and (2) baseline + 5 mol% NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> ammonium, and (3) baseline + 5 mol% PYR<sub>14</sub>TFSI ionic liquid.

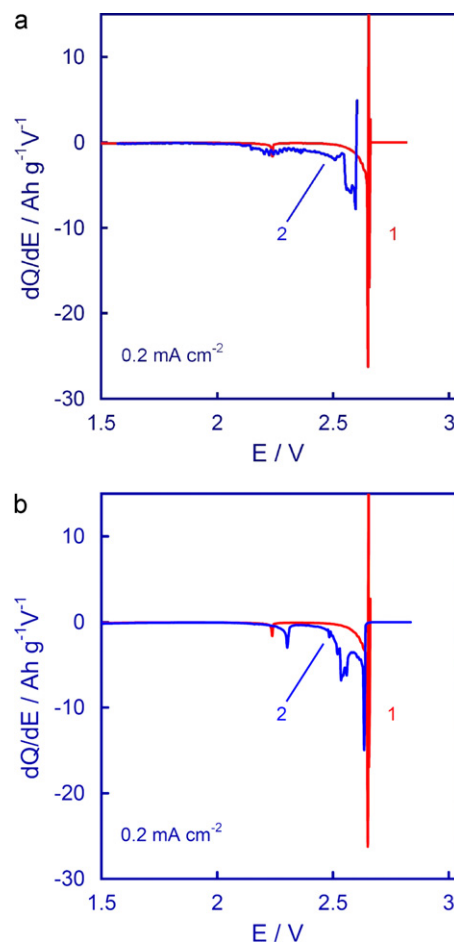
methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR<sub>14</sub>TFSI, a room temperature ionic liquid) as an alternative ammonium, and compare its discharge curve in Fig. 5. It is shown that both NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> and PYR<sub>14</sub>TFSI increase discharge capacity of Li/O<sub>2</sub> cells in different degrees. The geometric structure of ammonium cation affects discharge of Li/O<sub>2</sub> cells in two inverse manners. That is, the large cation volume (size) increases the solubility of ammonium peroxide, which facilitates oxygen reduction. However, the large cation reduces the amount of oxygen reduction products that can be deposited in the limited pores of air electrode when ammonium peroxide and ammonium oxide become the major products of oxygen reduction on the surface of carbon.

### 3.3. Role of ammonium in the discharge of Li/O<sub>2</sub> cell

To understand the role of quaternary ammonium in the discharge of Li/O<sub>2</sub> cells, we plot the differential capacities of two Li/O<sub>2</sub> cells without and with 5 mol% ammonium as the electrolyte additive against the cell voltage in Fig. 6. In the baseline electrolyte cell, there are two well-defined differential capacity peaks at 2.65 V and 2.22 V, respectively (see Curve-1 in Fig. 6a and b). These two peaks respectively correspond to Eqs. (1) and (3), of which the latter is much smaller and shows higher polarization than the former. This result is in good agreement with our previous observation with M-30 activated carbon, and it is believed to be associated with the non-conductive property of Li<sub>2</sub>O<sub>2</sub> [15,16]. However, in the cells with 5 mol% NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> or PYR<sub>14</sub>TFSI added, the differential capacity peaks become more complicated, showing multiple scattered peaks and higher differential capacity backgrounds, as indicated by Curve-2 in Fig. 6a and b. This significant difference can be attributed to the “phase transfer” catalytic effect of the quaternary ammonium cations on the reduction of Li<sub>2</sub>O<sub>2</sub> intermediate, which can be described as follows:



In this manner, the ammonium cation (M<sup>+</sup>) carries Li<sub>2</sub>O<sub>2</sub> from solid phase into solution phase, by forming slightly soluble ammonium peroxide (M<sub>2</sub>O<sub>2</sub>), where the reduction of peroxide anion (O<sub>2</sub><sup>2-</sup>) can occur smoothly. As a result of the “phase transfer” catalysis, polarization for the reduction of insoluble Li<sub>2</sub>O<sub>2</sub> is reduced. Meanwhile, this action is believed to facilitate the growth and dense deposition of Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>O particles on the surface of carbon, resulting in higher capacity.



**Fig. 6.** Plots of differential capacity versus cell potential difference for Li/O<sub>2</sub> cells with (1) baseline electrolyte consisting of 0.2 mol kg<sup>-1</sup> LiSO<sub>3</sub>CF<sub>3</sub> 1:3 PC/DME and (2) baseline + 5 mol% quaternary ammonium. (a) NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> and (b) PYR<sub>14</sub>TFSI.

## 4. Conclusions

As discussed above, the organic quaternary ammonium salts show significant effect on the discharge behavior of Li/O<sub>2</sub> cells. At low concentrations, the ammonium cations act as a “phase transfer catalyst” to facilitate the reduction of lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) intermediate into lithium oxide (Li<sub>2</sub>O) and favor the growth and dense deposition of oxygen reduction products (Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>O) by forming a slightly soluble ammonium peroxide (M<sub>2</sub>O<sub>2</sub>, M represents ammonium cation) intermediate. This function not only reduces the polarization of Li<sub>2</sub>O<sub>2</sub> reduction, but also increases the overall discharge capacity of a Li/O<sub>2</sub> cell. At high concentrations, part of the oxygen reduction products will be directly deposited in the form of M<sub>2</sub>O<sub>2</sub> or M<sub>2</sub>O. Due to much larger molar volume (size) of the ammonium cation than Li<sup>+</sup> ion, the amount that the oxygen reduction products can deposit on the surface of carbon is reduced. In this case, the ammonium reduces discharge capacity of Li/O<sub>2</sub> cells. In this work, we show that adding a 5 mol% ammonium (either NBu<sub>4</sub>SO<sub>3</sub>CF<sub>3</sub> or PYR<sub>14</sub>TFSI) is sufficient for the purpose of improving discharge capacity of Li/O<sub>2</sub> cells.

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